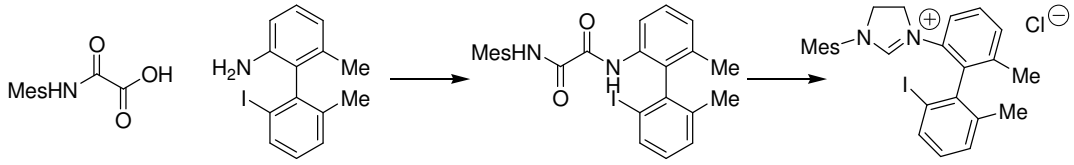
Materials and Methods. All reactions involving metal complexes were conducted in oven-dried glassware under a nitrogen atmosphere using standard glovebox techniques. Solvents were prepared by passage through alumina. All commercially obtained reagents were used as received. Organic reagents were purchased from Sigma-Aldrich and metal salts obtained from Strem. $NiClPh(PPh_3)_2$[1] and $NiBrMes(PPh_3)_2$[2] were prepared according to literature procedures. The synthesis of compound **1** is described elsewhere.[3] ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz, 75 MHz and 121 MHz respectively) or a Varian Inova 500 spectrometer (at 500 MHz, 125 MHz and 203 MHz respectively) and are reported relative to Me_4Si (δ 0.0) for ^1H and ^{13}C, and H_3PO_4 (δ 0.0) for ^{31}P. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C and ^{31}P NMR spectra are reported in terms of chemical shift.

***N*-(2,6-Diisopropylphenyl)-*N*-benzylidene-*N´*-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-ethylene diimine triphenylphosphine nickel(II) (2).** 1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolium chloride (**1**) (162 mg, 0.320 mmol, 1.00 equiv) and potassium hexamethyldisilazide (134 mg, 0.670 mmol, 2.10 equiv) were weighed together in a vial in the glovebox. THF (~10 mL) was added to the mixture of solids, providing a light yellow solution with a light precipitate. This was added to a round-bottomed flask and allowed to stir for ten minutes. At this point, a solution of $NiClPh(PPh_3)_2$ (223 mg, 0.320 mmol, 1.00 equiv) in THF (5 mL) was added, giving a dark green solution with precipitate. This solution was allowed to stir at room temperature for 1 hr and then was filtered through Celite. The solvent was removed under reduced pressure until ca. 2 mL remained. Pentane (~15 mL) was added and the solution was allowed to sit at -40 °C overnight, yielding a dark green solid (163 mg, 0.190 mmol, 59% yield). Crystals suitable for X-ray crystallography were grown by layering pentane over a concentrated solution of **2** in THF and storing this layered solution at –40 °C for two days. The ^1H NMR spectrum of **2** showed some broad peaks attributed to a fluxional process on the NMR timescale. This is most likely due to restricted rotation of the diisopropylphenyl and phenyl moieties, which are adjacent in the X-ray crystallographic structure. The ^{13}C NMR spectrum of **2** features many fewer resonances than expected. This may be due to the fact that several resonances may overlap, *e.g.* from the triphenylphosphine and adamantyl moieties. In addition, the fluxional processes described above may weaken some signals. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.56 (t, J = 9 Hz, 6 H), 7.32 (td, J = 1.5 Hz, 7.5 Hz, 2H), 7.23 (td, J = 1.5 Hz, 7.5 Hz, 6H), 7.16 (t, J = 7.5 Hz, 1H), 6.78 (t, J = 7 Hz, 1H), 6.4 (d, J = 1 Hz, 1H), 6.24 (d, J = 1 Hz, 1H), 4.76 (bs, 1H), 4.16 (bs, 1H), 3.38 (bs, 1H), 2.92 (bs, 2H), 2.26 (s, 3H), 1.92 (bs, 6H), 1.60 (bs, 3H), 1.38 (d, J = 11 Hz, 3H), 1.24 (bs, 12 H), 1.19 (d, J = 11.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 143.5, 135.1, 135.0, 134.9, 133.6, 133.3, 130.1, 130.0, 129.2, 128.5, 128.4, 128.2, 123.1, 113.4, 107.6, 68.0, 45.2, 41.3, 37.7, 36.6, 30.0, 21.8; ^{31}P NMR (121 MHz, C_6D_6): δ 22.6; HRMS: Calcd for $C_{56}H_{61}N_2ONi$ (M^+): 866.3875. Found 866.3835.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolyl mesityl triphenylphosphine nickel(II) (3). This complex was synthesized in a manner similar to that for **3**, using $NiBrMes(PPh_3)_2$ as the nickel source

(62% yield). Crystals suitable for X-ray crystallography were grown by layering pentane over a concentrated solution of **3** in THF and storing this layered solution at –40 °C for two days. The ^{1}H NMR spectrum of **3** showed some broad peaks attributed to a fluxional process on the NMR timescale. This is most likely due to restricted rotation of the diisopropylphenyl and mesityl moieties, which are adjacent in the X-ray crystallographic structure. Upon warming a C_6D_6 solution of **3** to 70 °C in the NMR spectrometer, the broad peaks began to coalesce. However, they did not become well-defined. It should be noted that at this elevated temperature, no further reaction, *i.e.* mesityl-group migration, followed by ring-expansion, was observed. ^{1}H NMR (500 MHz, C_6D_6): δ 8.47 (bs, 1H), 7.93 (bs, 1H), 7.76 (dd, *J* = 8 Hz, 11.5 Hz, 1H), 7.41-7.38 (m, 2H), 7.20 (t, *J* = 8 Hz, 2H), 7.06-6.98 (m, 6H), 6.94 (dd, *J* = 2 Hz, 8 Hz, 6H), 6.70 (bs, 1H), 6.47 (bs, 2H), 6.20 (bs, 2H), 6.12 (bs, 1H), 5.68 (bs, 1H), 4.42 (bs, 1H), 3.68 (bs, 1H), 3.38 (bs, 1H), 3.21 (bs, 1H), 2.99 (bs, 3H), 2.64 (s, 3H), 2.21 (bs, 3H), 2.06 (bs, 3H), 1.98 (s, 3H), 1.82 (bs, 6H), 1.71 (s, 3H), 1.53 (dd, *J* = 11.5 Hz, 27 Hz, 6H), 1.12 (bs, 3H), 0.58 (bs, 3H); ^{1}H NMR (500 MHz, C_6D_6): δ 195.4, 194.6, 158.2, 147.9, 144.5, 144.3, 141.1, 138.5, 136.8, 136.7, 135.8, 134.6, 134.5, 132.8, 132.8, 131.9, 131.3, 131.3, 129.2, 129.1, 129.0, 128.8, 123.9, 119.3, 117.8, 54.7, 54.7, 50.8, 41.2, 38.0, 37.7, 30.0, 21.9, 20.7; ^{31}P NMR (203 MHz, C_6D_6): δ 19.6; HRMS: Calcd for $C_{59}H_{67}N_2ONi$ (M^+): 908.4345. Found 908.4390.



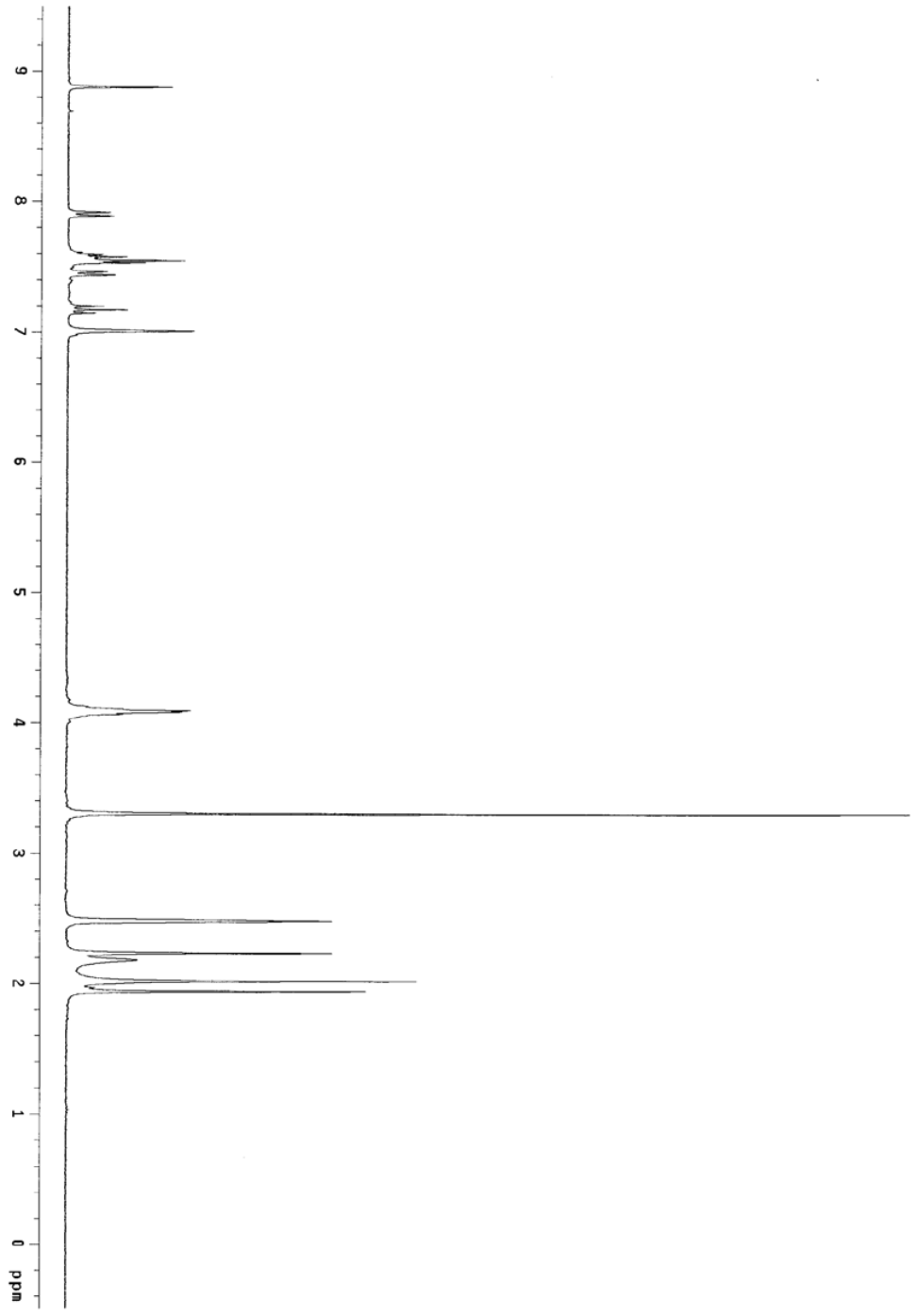
I II III 4

Dihydroimidazolium salt 4: To a suspension of carboxylic acid **I**[3] (2.29 g, 11.0 mmol, 1.05 equiv) in CH_2Cl_2 (10.5 ml) at 23 ºC is added carbonyl diimidazole (1.79 g, 11.0 mmol, 1.05 equiv) in one portion. The suspension is stirred until a clear solution is formed and CO_2 evolution has ceased (5–10 min). To this solution aniline **II**[4] (3.40 g, 10.5 mmol, 1.00 equiv) in CH_2Cl_2 (10.5 ml) is added and the solution is stirred for 16 h at 23 ºC. The solids formed are filtered off, washed with HCl (2 M), NaOH (2 M), and water to afford the diamide **III** as a colorless solid in 61 % yield. Melting Point (toluene): mp 258 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.85 (s, 1H), 8.68 (s, 1 H), 8.36 (d, J = 8.0 Hz, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.42 (dd, J = 8.0, 8.0 Hz, 1 H), 7.32 (d, J = 7.7 Hz, 1 H), 7.18 (d, J = 7.7 Hz, 1 H), 7.02 (dd, J = 7.7, 7.7 Hz, 1 H), 6.87 (s, 2 H). Mass Spectrometry HRMS-FAB+ (m/z): Calcd for $C_{25}H_{26}N_2O_2I$, 513.1039. Found, 513.1035. To diamide **III** (2.60 g, 5.07 mmol, 1.00 equiv) in a pressure vessel (250 ml) is added BH_3·THF in THF (1.0 M, 41 ml, 41 mmol, 8.0 equiv). The pressure vessel is sealed and the solution is heated at 75 ºC for 20 h. After cooling the pressure vessel is opened (CAUTION: gas evolution under pressure) and the colorless solution is poured onto methanol (100 ml). To this solution is added HCl (conc., 1.0 ml) and the solution is concentrated in vacuo. The resulting solid is dissolved in methanol (100 ml) and concentrated in vacuo. This procedure is repeated twice to afford a colorless solid. This solid is suspended in triethylorthoformate (26 ml) and the suspension is placed in a preheated oil bath at 125 ºC for a total time of 25 min (after initial dissolution, a

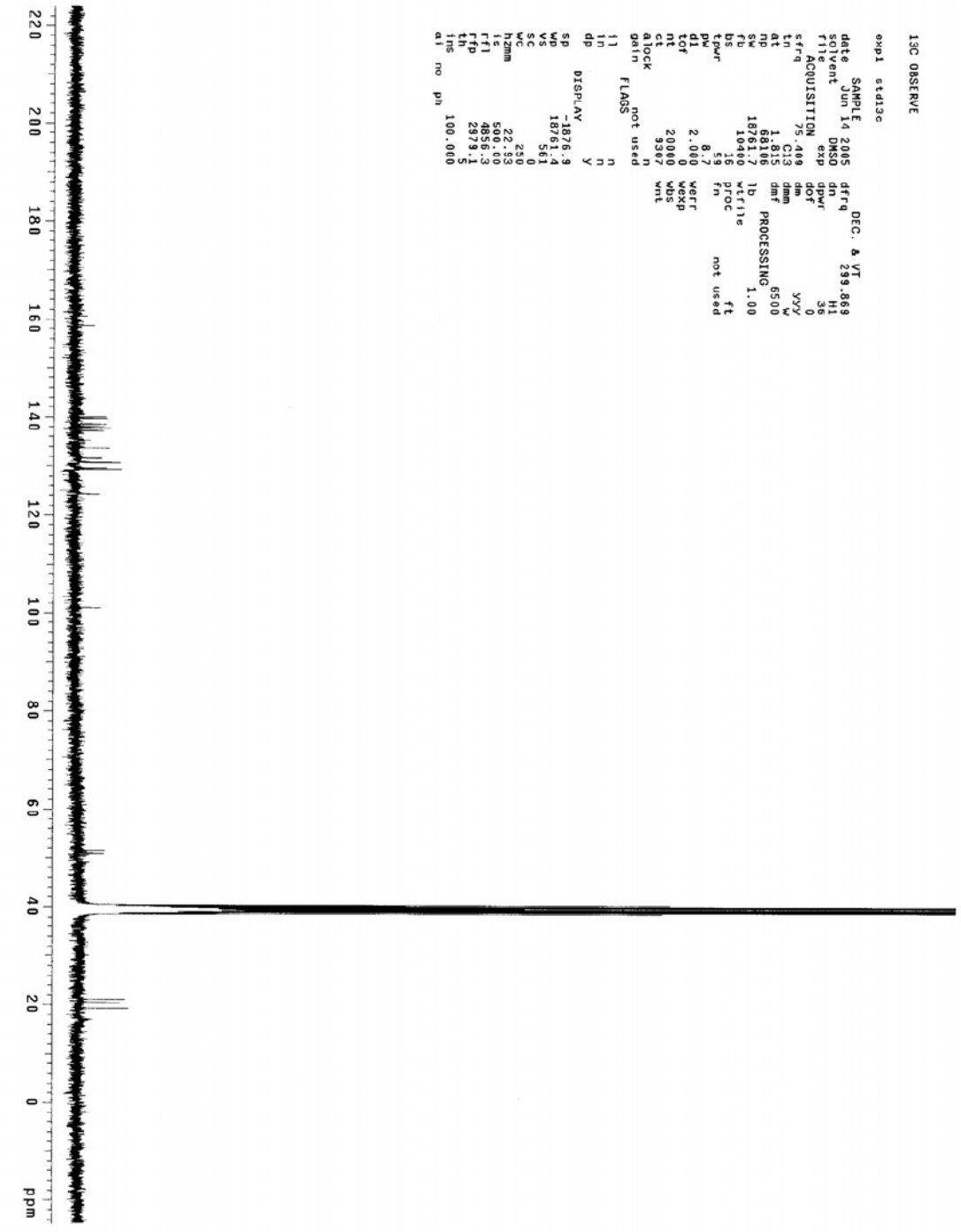
suspension is formed after 5 min). To the suspension is added diethylether (10 ml) and the solids are filtered off and washed with diethylether extensively to afford the title compound as colorless solid in 52 % yield, 2 steps.

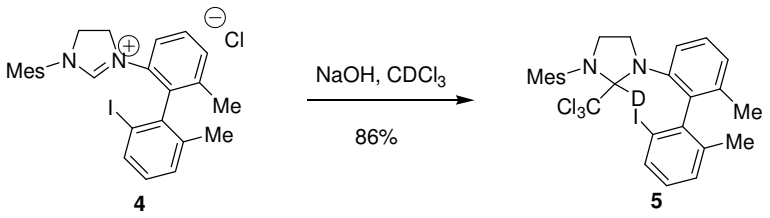
Melting Point (Et_2O): mp 265 ºC (decomposition). ^{1}H NMR (300 MHz, DMSO-d6) δ: 8.89 (s, 1H), 7.91 (d, J = 7.7 Hz, 1 H), 7.62–7.55 (m, 3 H), 7.46 (d, J = 7.7 Hz, 1 H), 7.18 (dd, J = 7.7, 7.7 Hz, 1 H), 7.02 (s, 2 H), 4.12–4.08 (m, 4 H), 2.25 (s, 3 H), 2.19 (s, 3 H), 2.02 (s, 3 H), 2.03 (s, 3 H), 1.95 (s, 3 H). ^{13}C NMR (75 MHz, DMSO-d6) δ: 158.6, 139.9, 139.6, 138.5, 138.1, 137.8, 137.1, 135.2, 133.7, 131.5, 130.7, 130.7, 129.5, 129.3, 124.2, 101.1, 51.4, 50.9, 21.1, 20.5, 19.2. Mass Spectrometry HRMS-FAB+ (m/z): Calcd for $C_{26}H_{28}N_2I$, 495.1298. Found, 495.1322.

Compound **4**



Compound **4**

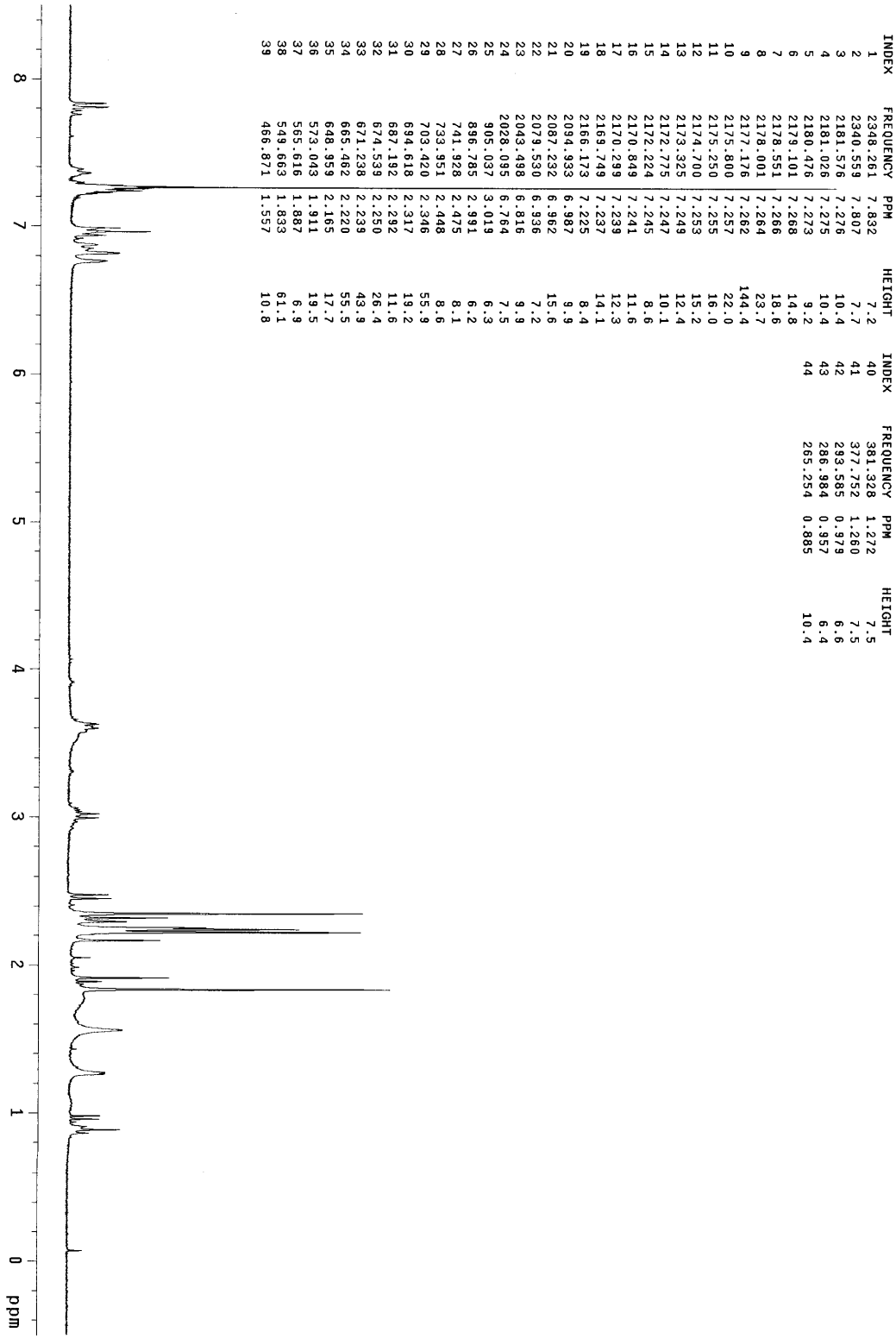

13C OBSERVE
expl stdl3c
SAMPLE
date Jun 14 2005
solvent DMSO
file exp
ACQUISITION
sfrq 75.409
tn C13
at 1.815
np 68106
sw 18761.7
fb 10400
bs 16
tpwr 48
pw 8.7
pw1 2.000
d1 1.000
tof 0
nt 20000
ct 9307
alock n
gain n
FLAGS
il n
in n
dp y
DISPLAY
sp -1876.9
wp 18761.4
vs 561
sc 0
wc 250
hzmm 22.93
is 500.00
rfl 4856.3
rfp 2979.1
th 2979.5
ins 100.000
ai no pn
dfrq DEC. & VT
dn 299.869
dpwr H1
dof 36
dm 0
dmm yyy
dmf w
PROCESSING 6500
lb 1.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
220
200
180
160
140
120
100
80
60
40
20
0
ppm



4 **5**

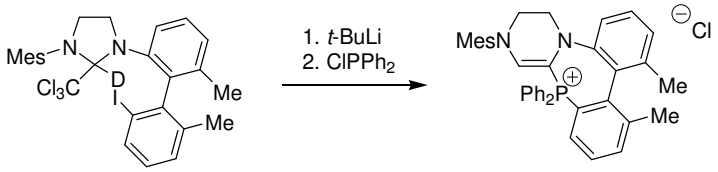
To fine ground NaOH (2.26 g, 56.5 mmol, 20.0 equiv) in $CDCl_3$ (14 ml) prestirred for 2 min is added dihydroimidazolium salt **4** (1.50 g, 2.83 mmol, 1.00 equiv) and the suspension is vigorously stirred at 20 ºC for 1 h. This suspension is poured onto CH_2Cl_2/icewater. The aqueous phase is extracted with CH_2Cl_2 (2 × 20 ml). The combined organic layers are washed with brine, dried over Na_2SO_4 and concentrated in vacuo to afford a colorless solid. This residue is purified by chromatography on silica gel eluting with hexane/EtOAc (20:1) to afford the title compound as a 3:1 mixture of diastereomers as a colorless foam in 86 % yield. The diastereomers were not separated due to the instability of the product, instead the product was used immediately in the subsequent step. Integrals for the ^1H NMR spectrum are not given, because of the product mixture. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.82 (d, J = 7.7 Hz), 7.76 (d, J = 7.7 Hz), 7.36–7.28 (m), 6.99–6.76 (m), 3.62–3.51 (m), 3.05–2.93 (m), 2.48, 2.45, 2.35, 2.32, 2.29, 2.25, 2.24, 2.20, 1.91, 1.83. Mass Spectrometry HRMS-FAB+ (m/z): Calcd for $C_{27}H_{28}N_2{}^2HCl_3I$, 614.0505. Found, 614.0524.

Compound **5**



INDEX	FREQUENCY	PPM	HEIGHT
1	2348.261	7.832	7.2
2	2340.559	7.807	7.7
3	2181.576	7.276	10.4
4	2181.026	7.275	10.4
5	2180.476	7.273	9.2
6	2179.101	7.268	14.8
7	2178.551	7.266	18.6
8	2178.001	7.264	23.7
9	2177.176	7.262	144.4
10	2175.800	7.257	22.0
11	2175.250	7.255	16.0
12	2174.700	7.253	15.2
13	2173.325	7.249	12.4
14	2172.775	7.247	10.1
15	2172.224	7.245	8.6
16	2170.849	7.241	11.6
17	2170.299	7.239	12.3
18	2169.749	7.237	14.1
19	2166.173	7.225	8.4
20	2094.933	6.987	9.9
21	2087.232	6.962	15.6
22	2079.530	6.936	7.2
23	2043.498	6.816	9.9
24	2028.095	6.764	7.5
25	905.037	3.019	6.3
26	896.785	2.991	6.2
27	741.928	2.475	8.1
28	733.951	2.448	8.6
29	703.420	2.346	55.9
30	694.618	2.317	19.2
31	687.192	2.292	11.6
32	674.539	2.250	26.4
33	671.238	2.239	43.9
34	665.462	2.220	55.5
35	648.959	2.165	17.7
36	573.043	1.911	19.5
37	565.616	1.887	6.9
38	549.663	1.833	61.1
39	466.871	1.557	10.8

INDEX	FREQUENCY	PPM	HEIGHT
40	381.328	1.272	7.5
41	377.752	1.260	7.5
42	293.585	0.979	6.6
43	286.984	0.957	6.4
44	265.254	0.885	10.4

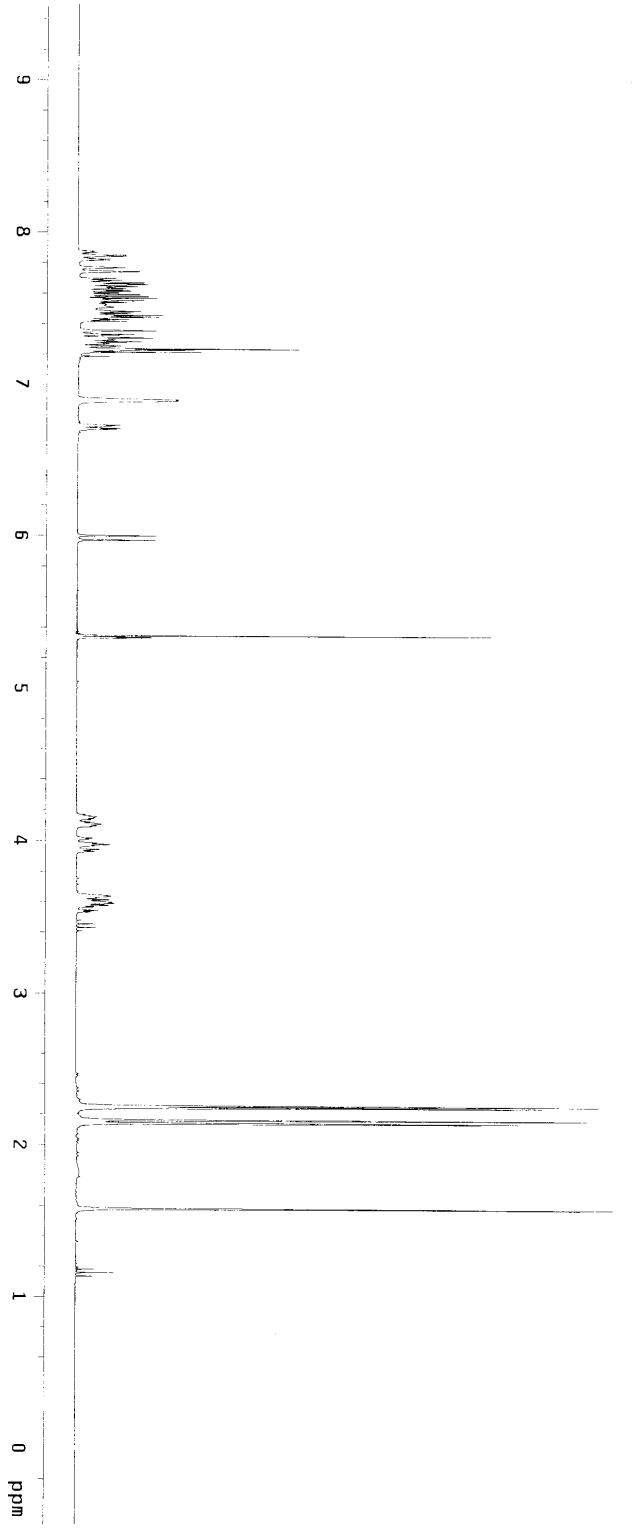


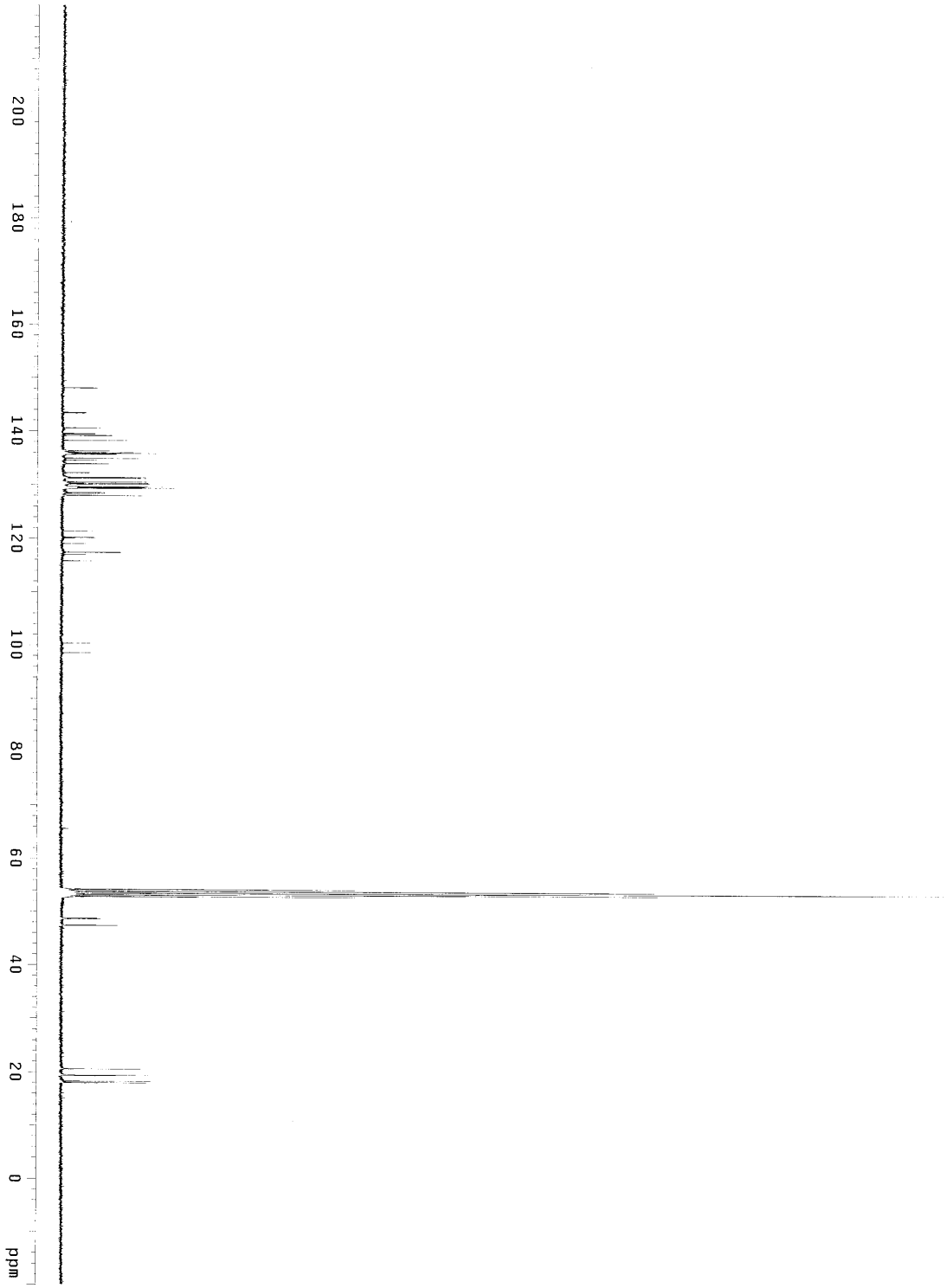
5 **7**

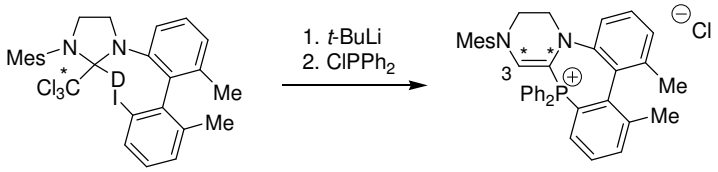
Phosphonium salt 7: To the mixture of chloroform adducts **5** (725 mg, 1.18 mmol, 1.00 equiv) at –78 ºC is added THF (6.0 ml) (**5** decomposes if dissolved in THF at room temperature). The solution is cooled to –100 ºC and *tert*-butyllithium in pentane (1.60 M, 1.55 ml, 2.48 mmol, 2.10 equiv) is added. After 5 min at –100 ºC, chlorodiphenylphosphine (313 mg, 1.42 mmol, 1.20 equiv, 254 µl) is added and the solution is warmed to –40 ºC and stirred at this temperature for 2.5 h. To this solution at –40 ºC is added HCl in diethylether(1.0 M, 2.4 ml, 2.4 mmol, 2.0 equiv) followed by methanol (300 µl). The solution is poured onto CH_2Cl_2/HCl (1 M). The aqueous phase is extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layers are washed with brine, dried over Na_2SO_4 and concentrated in vacuo to afford a yellow solid. This residue is purified by chromatography on silica gel eluting with CH_2Cl_2/MeOH (9:1) to afford the title compound as pale yellow crystals in 51 % yield.

Melting Point (CH_2Cl_2/pentane): mp 275 ºC (decomposition). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.85–7.82 (m, 1 H), 7.77–7.74 (m, 1 H), 7.70–7.42 (m, 8 H), 7.36–7.19 (m, 5 H), 6.90–6.89 (m, 2 H), 6.73–6.71 (m, 1 H), 5.99 (d, *J* = 8.5 Hz, 1 H), 4.17–4.09 (m, 1 H), 4.02–3.93 (m, 1 H), 3.64–3.53 (m, 2 H), 2.25 (s, 3 H), 2.24 (s, 3 H), 2.16 (s, 3 H), 2.14 (s, 3 H), 2.58 (s, 3 H). ^{13}C NMR (74 MHz, CD_2Cl_2, coupling constants to ^{31}P given for established doublets only, other signals are reported as peaks) δ: 143.5, 143.3, 140.5, 139.5, 139.4, 139.1, 138.2, 136.3, 136.2, 136.0, 135.8, 138.8, 135.7, 134.9, 134.9, 134.9, 134.5, 133.9, 133.9, 132.2, 132.2, 131.4, 131.2, 130.5, 130.3, 130.1, 129.6, 129.5, 129.5, 129.4, 129.3, 128.5, 128.4, 128.0, 121.3, 120.2, 120.1, 119.0, 117.4, 116.9, 115.8, 99.4 (d, *J* = 136.0 Hz), 48.6 (d, *J* = 7.7 Hz), 47.4, 20.6, 19.4, 19.3, 18.2, 18.0. ^{31}P NMR (121 MHz, CD_2Cl_2) δ: 19.1. Mass Spectrometry HRMS-FAB+ (m/z): Calcd for $C_{39}H_{38}N_2P$, 565.2773. Found, 565.2746. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 267284.

Compound **7**



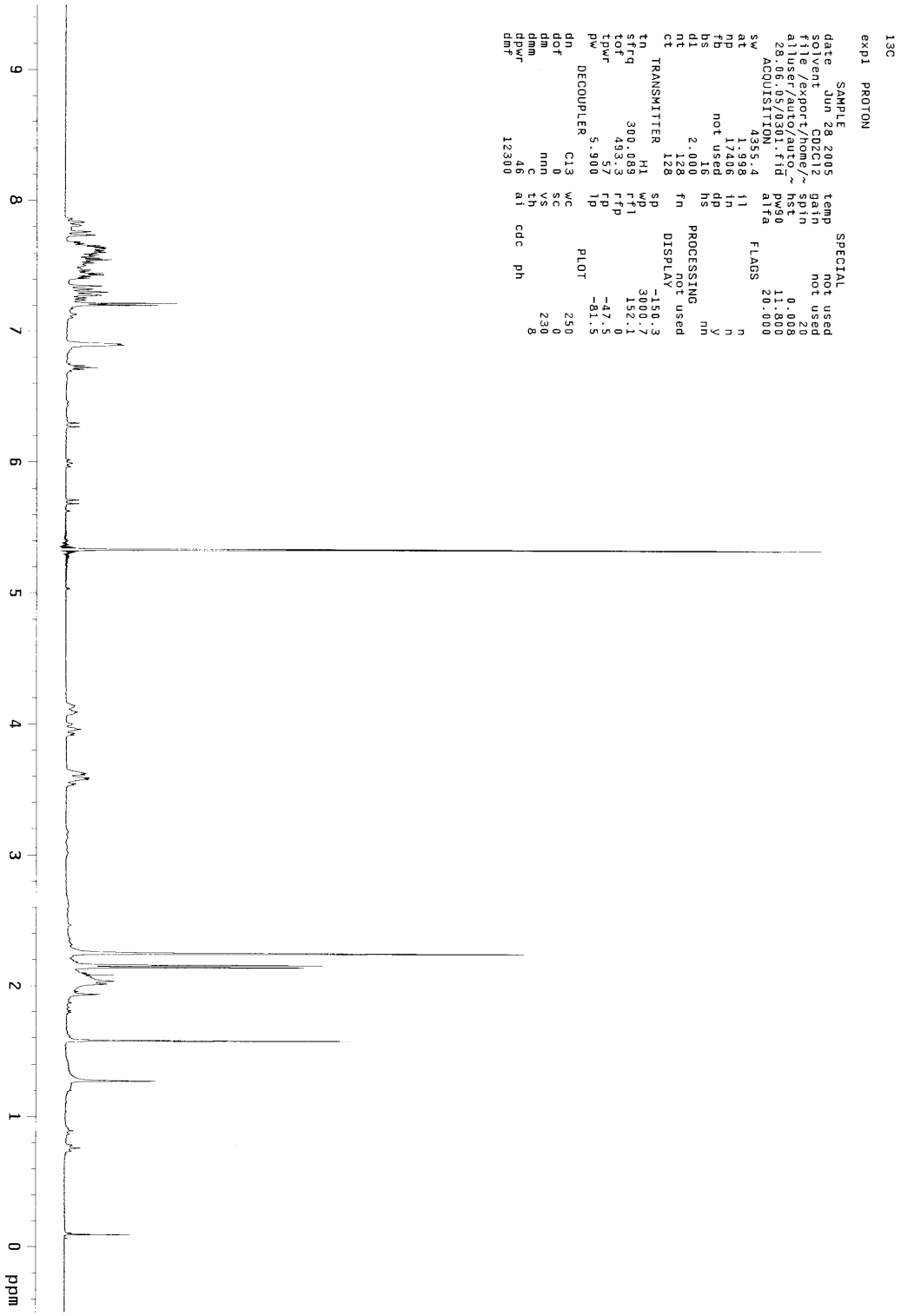

200
180
160
140
120
100
80
60
40
20
0
ppm

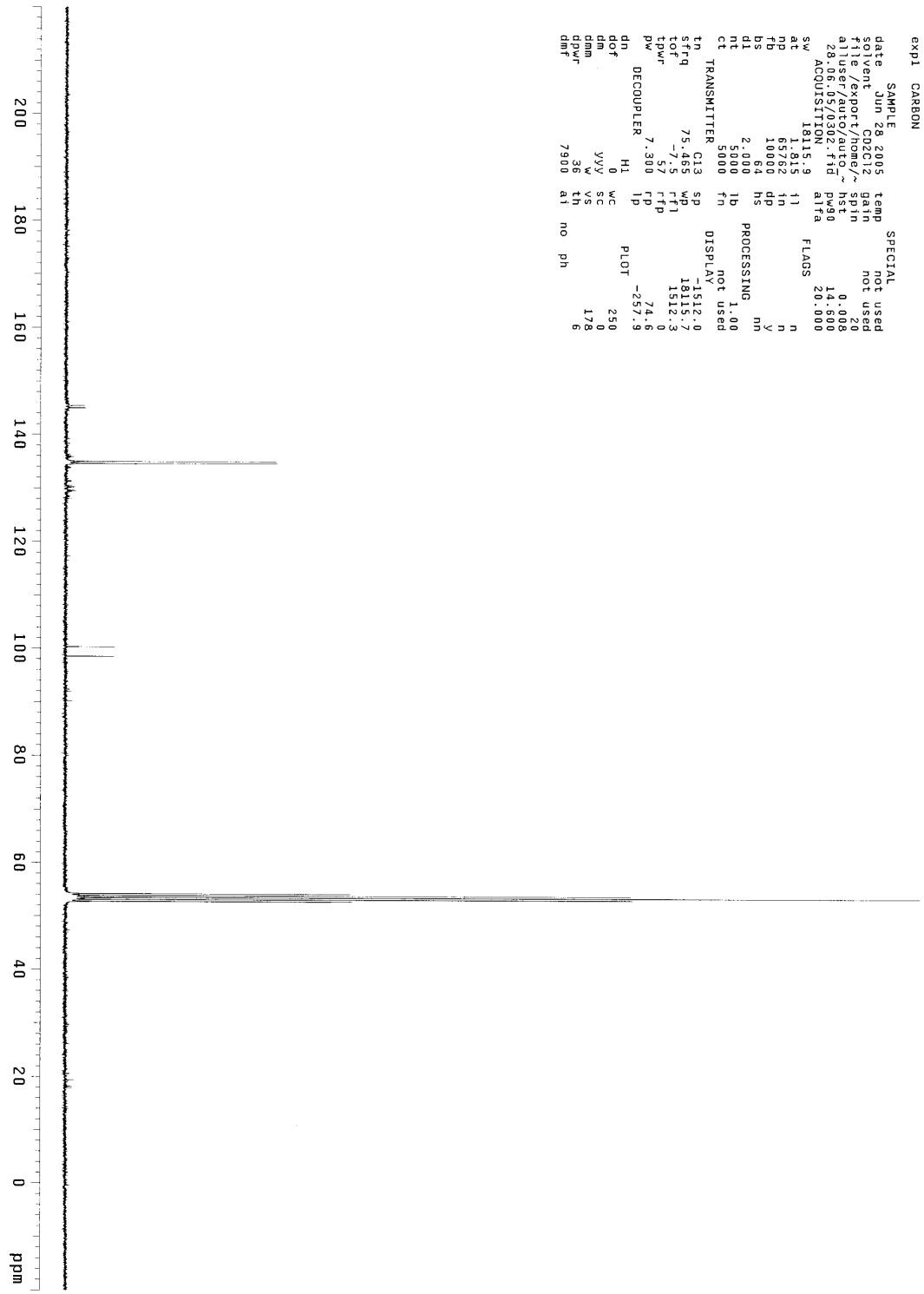


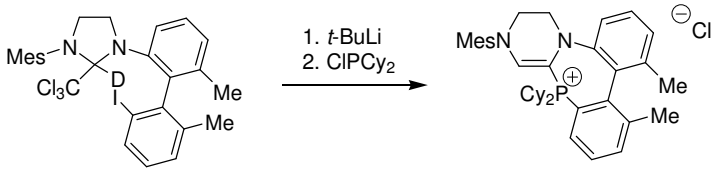
5l **7l**

When using ^{13}C labeled chloroform, in the preparation of **7l**, the ^{13}C label in **7l** is found in ring positions 2 and 3 as a 1:2 ratio. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 5.99 (dd, $^{1}J_{HC}$ = 174.9 Hz, $^{3}J_{HP}$ = 8.5 Hz), 5.99 (dd, $^{2}J_{HC}$ = 8.5 Hz, $^{3}J_{HP}$ = 8.5 Hz). ^{13}C NMR (74 MHz, CD_2Cl_2) δ: 134.7 (d, $^{2}J_{CP}$ = 28.5 Hz), 99.4 (d, $^{1}J_{CP}$ = 136.0 Hz). Mass Spectrometry HRMS-FAB+ (m/z): Calcd for $C_{38}H_{38}N_2{}^{13}CP$, 566.2806. Found, 566.2800.

Compound **7l**


13C
exp1 PROTON
SAMPLE SPECIAL
date Jun 28 2005 temp not used
solvent CD2Cl2 gain not used
file /export/home/~ spin 20
alluser/auto/auto_~ hst 0.008
28.06.05/0301.fid pw90 11.800
ACQUISITION 20.000
4355.4 fl FLAGS
1.998 in n
17406 dp n
not used hs y
16 nn
2.000 PROCESSING
128 fn not used
128 DISPLAY
TRANSMITTER -150.3
H1 wp 3000.7
300.089 rfl 152.1
493.3 rfp 0
57 rp -47.5
5.900 lp -81.5
DECOUPLER PLOT
C13 wc 250
0 sc 0
nnn vs 230
c th 8
46 ai cdc ph
12300
dn
dof
dm
dmm
dpwr
dmf
9
8
7
6
5
4
3
2
1
0
ppm

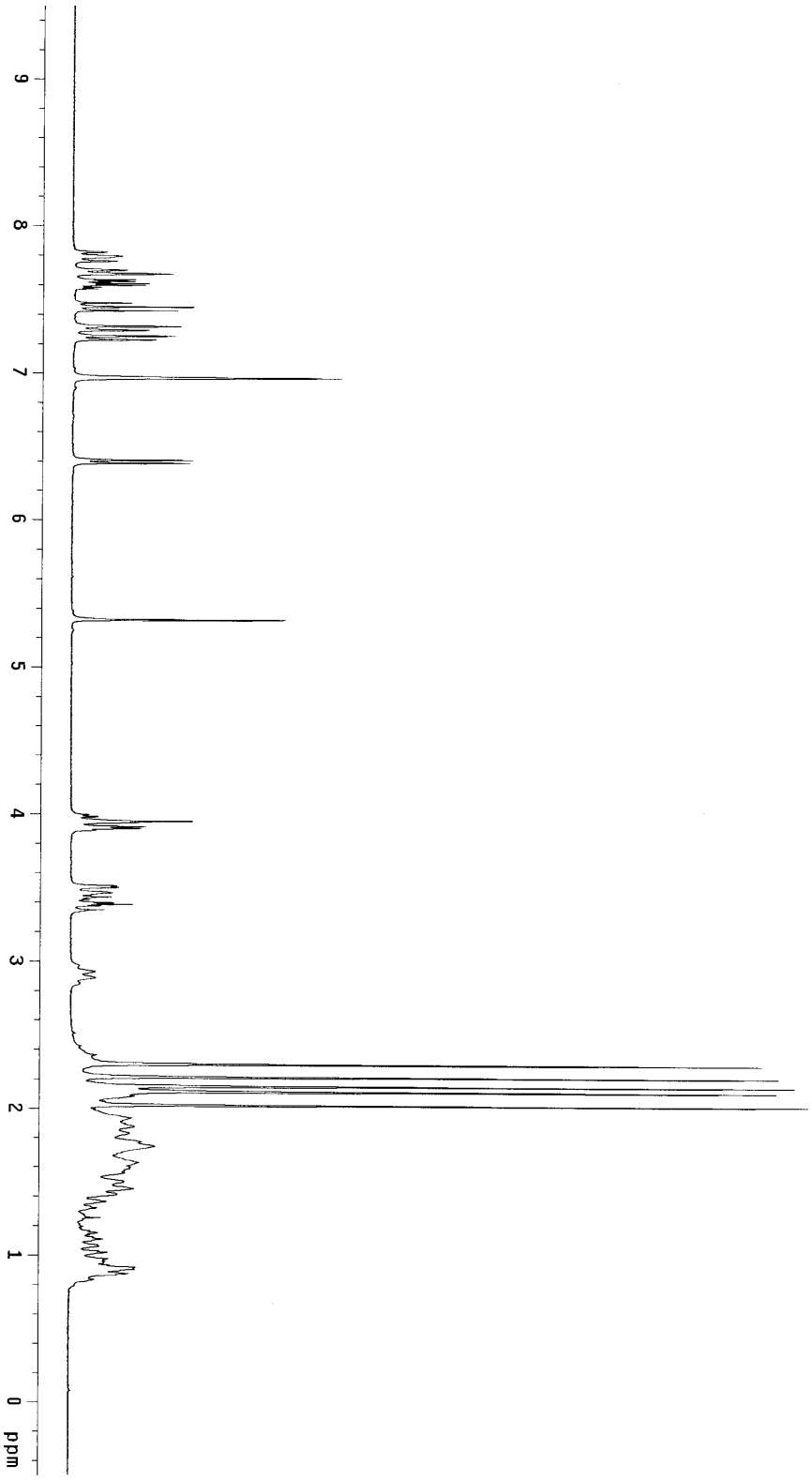

13C
exp1 CARBON
SAMPLE
date Jun 28 2005
solvent CD2Cl2
file /export/home/~
alluser/auto/auto_
28.06.05/0302.fid
ACQUISITION
sw 18115.9
at 1.815
np 65762
fb 10000
bs 64
d1 2.000
nt 5000
ct 5000
TRANSMITTER
tn C13
sfrq 75.465
tof -7.5
tpwr 57
pw 7.300
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 36
dmf 7900
SPECIAL
temp not used
gain not used
spin 20
hst 0.008
pw90 14.600
alfa 20.000
FLAGS
in n
dp n
hs y
PROCESSING
lb nn
fn 1.00
not used
DISPLAY
sp -1512.0
wp 18115.7
rfl 1512.3
rfp 0
rp 74.6
lp -257.9
PLOT
wc 250
sc 0
vs 178
th 6
al no ph
200
180
160
140
120
100
80
60
40
20
0
ppm

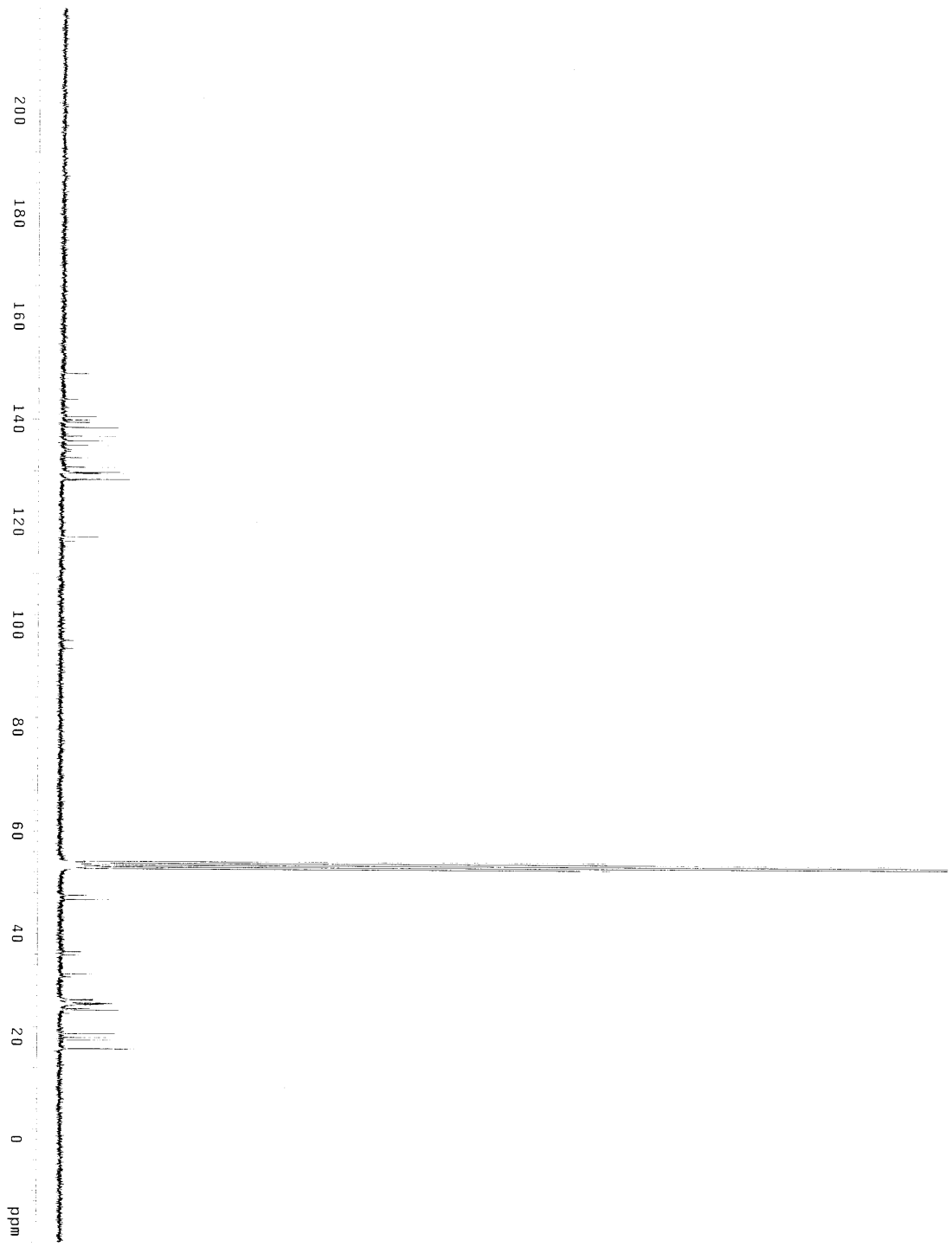


5 **IV**

Phosphonium salt IV: The phosphonium salt **IV** has been prepared analogously to **7**. Melting Point (CH_2Cl_2/pentane): mp 306 ºC (decomposition). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.79 (dd, *J* = 8.9, 8.3 Hz, 1 H), 7.69 (d, *J* = 7.7 Hz, 1 H), 7.60 (ddd, *J* = 7.7, 7.7., 3.3 Hz, 1 H), 7.45 (dd, *J* = 8.0, 7.7 Hz, 1 H), 7.31 (d, *J* = 7.7 Hz, 1 H), 7.24 (d, *J* = 7.4 Hz, 1 H), 6.97 (s, 2 H), 6.40 (d, *J* = 6.31 Hz, 1 H), 3.99–3.89 (m, 2 H), 3.51–3.35 (m, 2 H), 2.91 (q, *J* = 12.4 Hz, 1 H), 2.36–0.84 (m, 21 H), 2.30 (s, 3 H), 2.21 (s, 3 H), 2.15 (s, 3 H), 2.11 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR (74 MHz, CD_2Cl_2, coupling constants to ^{31}P given for established doublets only, other signals are reported as peaks) δ: 148.9, 143.9, 143.8, 140.4, 139.9, 139.8, 139.3, 138.4, 136.7, 135.8, 135.7, 134.9, 132.6, 130.7, 129.7, 129.7, 129.5, 129.5, 128.4, 128.2, 117.1, 116.2, 115.2, 96.2 (d, *J* = 116.4 Hz), 47.5 (d, *J* = 6.9 Hz), 36.2 (d, *J* = 49.2 Hz), 31.9 (d, *J* = 41.5 Hz), 27.3, 27.3, 27.1, 26.7, 26.5, 26.5, 26.4, 26.3, 26.0, 25.5, 25.2, 20.7, 19.9, 19.4, 17.8, 17.7. ^{31}P NMR (121 MHz, CD_2Cl_2) δ: 27.7. Mass Spectrometry HRMS-FAB+ (m/z): Calcd for $C_{39}H_{50}N_2P$, 577.3712. Found, 577.3727.

Compound **IV**




200
180
160
140
120
100
80
60
40
20
0
ppm

[1] Zeller, A.; Herdtweck, E.; Strassner, T. *Eur. J. Inorg. Chem.* **2003**, *9*, 1802–1806.
[2] Coronas, J. M.; Muller, G.; Rocamora, M.; Miravitlles, C.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1985**, *11*, 2333–2341.
[3] Waltman, A. W.; Grubbs, R. H. *Organometallics* **2004**, *23*, 3105–3107.
[4] Angeletti, A. *Gazz. Chim. Ital.* **1933**, *63*, 145–151.